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THE EFFECT OF CYANURIC ACID, A CHLORINE STABILIZER, ON TRIHALOMETHANE FORMATION

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16. ABSTRACT

Cyanuric acid, used commonly in swimming pools to stabilize chlorine, was investigated in an attempt to control trihalomethane (THM) formation in filtered river water. At 7.5:1 molar ratio, applied cyanuric acid to applied chlorine, THM formation was reduced by 29 per cent. The reduction diminished with decreasing molar ratio and increasing pH, both of which promoted higher free chlorine residuals. A model was employed to differentiate between free chlorine and chlorinated isocyanurates. At 7.5:1 in bromide-spiked water, THM formation was reduced only 9 per cent and formation of brominated THM species was favored; increasing molar ratio favored increasing bromoform formation. The data could be explained, in part, by the classical haloform reaction. Cyanuric acid probably holds little promise for THM control in drinking water treatment.

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INTRODUCTION

Cyanuric acid (Figure 1) has been widely used as a stabilizer of free chlorine in swimming pool disinfection since the mid 1950's.[1] When chlorine and cyanuric acid are mixed in solution, mono-, di- and trichloroisocynaurate are formed, depending on pH and concentration. Cyanuric acid acts as a reservoir for free chlorine in solution; as free chlorine is consumed, more free chlorine is released from chlorinated isocyanurates.[2] The equilibrium is:

$$H_3Cy + xHOCl \rightleftharpoons Cl_xH_{3-x}Cy + xH_2O \qquad (1)$$

The interactions of cyanuric acid and its chlorinated derivatives are very complex and include 12 equilibria expressions in addition to the equilibria of aqueous chlorine.[3] The time required to reach equilibrium between free chlorine and cyanuric acid is less than one minute.[2] Studies of swimming pools indicate that chlorinated isocyanurates are at least as effective as chlorine in bactericidal efficiency.[1,4,5]

The objective of this study was to investigate the effect of cyanuric acid on trihalomethane (THM) formation in potable water. Based on the classic haloform reaction[6] as a mechanism of THM formation, no reduction in THM concentration would be expected since the rate determining step is the conversion of the methyl ketone from the keto to enol form. However, if the mechanism of THM formation were chlorine dose dependent, it would be expected

that the addition of cyanuric acid would inhibit THM formation because of the reservoir effect of cyanuric acid with chlorine (Equation 1).

EXPERIMENTAL

Ohio River water was studied under two conditions. First, the effect of cyanuric acid on THM formation in river water was examined. Second, the effect of cyanuric acid on THM formation in bromide-spiked river water was studied.

River Water

Ohio River water was filtered through anthracite/sand filters using the pilot plant facility of the U.S. EPA Drinking Water Research Division, Cincinnati, Ohio. The filtered river water was buffered at the appropriate pH with a phosphate buffer for a final buffer strength of 0.004 M. Cyanuric acid (Kodak reagent grade) was added to the buffered water which was subsequently chlorinated (13 mg/L) with an appropriate aliquot of stock chlorine solution. The stock chlorine was prepared by bubbling chlorine gas through distilled water. Samples were stored head-space free at room temperature. After storage, samples were collected in head-space free vials with Teflon®-lined septa for THM analysis. The THM reaction was stopped by the addition of sodium thiosulfate. At the time of collection, pH and residual chlorine were measured. Chlorine species were measured by a DPD titration procedure.[7] Preserved samples were stored at 20°C in the dark prior to

analysis. Trihalomethanes were measured by a purge and trap gas chromatographic procedure.[8]

Bromide-Spiked River Water

After filtered river water was spiked with bromide (chlorine: bromide = 22:1 molar ratio), the procedures described above were carried out.

RESULTS AND DISCUSSION

Trihalomethane Formation in River Water

Unchlorinated river water had a total trihalomethane (TTHM) concentration below the detection level. Chlorinated river water produced a characteristic TTHM formation curve[9] reaching 0.756 umoles/L at 7 days (Figure 2). The mean distribution of THM species was 76%, 21%, 4% and 0.7% for chloroform, bromodichloromethane, dibromochloromethane, and bromoform, respectively.

The addition of cyanuric acid (175 mg/L) in a 7.5:1 molar ratio* to chlorine inhibited TTHM formation by a mean 29% each day over a 13 day reaction period (Figure 2). However, increasing the concentration of cyanuric acid (15:1 molar ratio) showed no further reduction in TTHM concentration. The distribution of THM compounds was the same with or without cyanuric acid.

*The molar ratio is defined as the ratio of the applied cyanuric acid concentration and the applied chlorine concentration.

Because of the reservoir effect and the rapidity with which chlorinated isocyanurates liberate free chlorine as free chlorine is consumed, chlorinated isocyanurates appear as false positive free chlorine in common analytic procedures.[10,11] Thus, in a cyanuric acid-aqueous chlorine system, these procedures measure both free chlorine and chlorinated isocyanurates. For purposes of this study, the sum of these species was termed total chlorine concentration since little or no combined chlorine was detected. To differentiate between free chlorine and chlorinated isocyanurates, the model and equilibrium constants of O'Brien[3] were used. Model calculations were made based on the pH and the concentrations of applied chlorine and cyanuric acid.

At pH 7, and at molar ratios of 7.5:1 and 15:1, the model predicted less than 0.1 mg/L free chlorine was present at any time, whereas free chlorine residuals in the non-cyanuric acid treated water exceeded 6 mg/L.

To futher investigate the effect of molar ratio, cyanuric acid was added at 2, 100 and 175 mg/L concentrations providing molar ratios of 0.08:1, 4.3:1 and 7.5:1. Little difference was observed between those treated at 4.3:1 and 7.5:1 ratios: 24% reduction in TTHM concentrations after seven days, in both cases, (Figure 3). However, at the 0.08:1 ratio, the TTHM concentration was inhibited only 7%. The model predicted the free chlorine concentration was 5.6 mg/L at the lowest molar ratio (as expected,

because of a stoichiometric excess of chlorine), compared to less than 0.1 mg/L free chlorine at the higher molar ratios.

At seven days, O'Brien's model indicated that at molar ratios below 1.1:1, the amounts of free chlorine in the system would increase dramatically (Figure 3). With most of the total chlorine present as free chlorine, the levels of TTHM were comparable to those if no cyanuric acid was present.

The effect of pH was also studied. THM concentrations were measured after a seven day reaction time at pH 6, 7, 8 and 9. River water treated with 13 mg/L chlorine showed an increasing TTHM concentration with increasing pH (Figure 4), in agreement with the literature.[12] The distribution of THM species was similar to that discussed earlier. With the addition of cyanuric acid at a molar ratio of 7.5:1, TTHM concentration increased with increasing pH. At pH 6, 7, 8 and 9, TTHM concentration were respectively, 24%, 23%, 22% and 6% less than the TTHM concentrations in the system containing no cyanuric acid. Based on O'Brien's model, the free chlorine was less than 0.2 mg/L at pH 6, 7, 8, and increased to 0.75 mg/L at pH 9.

The large difference in the concentration of chlorine present (6 mg/L in non-cyanuric acid treated water, compared to less than 0.1 mg/L calculated for cyanuric acid treated water) and only 29% difference in TTHM concentration can be explained by the classic haloform reaction for f[illegible]tion of THMs. Since the rate determining step in this react[illegible] is the conversion of the methyl ketone

substrate from the keto to the enol form, the overall reaction rate for chloroform formation is independent of chlorine concentration. However, not all precursor material in natural waters are methyl ketones and these may react by a mechanism other than the classic haloform reaction where the rate determining step may be chlorine dose dependent thus accounting for some observed decrease in TTHM concentration when cyanuric acid was present.

THM Formation in Bromide-Spiked River Water

River water spiked with 0.67 mg bromide/L and treated with chlorine reached a TTHM concentration of 1.17 umoles/L after seven days reaction time with larger concentrations of brominated THMs caused by bromide addition. The application of cyanuric acid in a 7.5:1 molar ratio with applied chlorine in the bromide-spiked water resulted in a TTHM concentration of 1.06 umoles/L after seven days (Figure 5). This shows only a 9% reduction in TTHM concentration with the addition of cyanuric acid.

In bromide-spiked river water treated with chlorine only, the mean distribution of species was 8% chloroform, 23% bromodichloromethane, 46% dibromochloromethane and 20% bromoform. However, with the application of cyanuric acid (molar ratio 7.5:1) the mean distribution changed to 1%, 10%, 35% and 53%, respectively. (In the river water containing naturally occurring levels of bromide no such change in species distribution was observed with the addition of cyanuric acid. This might be explained, however, by the low

levels of brominated species formed and analytic imprecision in that range.)

O'Brien's model does not account for chlorine's oxidation of bromide to bromine. No attempt was made to modify the model. While the relative amounts of free chlorine and free bromine were not known, increasing amounts of cyanuric acid favored an increase of brominated species. When cyanuric acid was added at concentration of 0, 2, 25, 100 and 175 mg/L to bromide-spiked river water and subsequently chlorinated giving molar ratios of 0:1, 0.08:1, 1.1:1, 4.3:1, and 7.5:1, the TTHM concentrations were 0.929, 1.02, 0.990, 0.936, and 0.924 umoles/L, respectively (Figure 6). The distribution of species at 0:1 and 0.08:1, found dibromchloromethane the predominant species - similar to the system that received no cyanuric acid. At 1.1:1, 4.3:1 and 7.5:1, the predominant species was bromoform.

The TTHM concentrations of bromide-spiked river water were measured after seven days at varying pH (Figure 7). The mean distribution of THM species was 6% chloroform, 25% bromodichloromethane, 46% dibromochloromethane and 24% bromoform. After treatment with cyanuric acid, the mean distribution was 1%, 12%, 36% and 55%, respectively. While TTHM concentrations were higher in the cyanuric acid treated system at pH 6 and 7, they decreased in the same system at pH 8 and 9 (Figure 7).

The data for the bromide-spiked water can also be explained by the classic haloform reaction as a mechanism of THM formation.

Chlorine and bromine were present at all times and were available for THM formation once the enol form of the methyl ketone was present. Therefore, very little difference in total THM concentration was observed with the addition of cyanuric acid. In the cyanuric acid treated water, the ratio of HOBr to HOCl is higher than in the non-cyanuric acid treated water because the HOCl concentration was reduced because of its equilibrium with chlorinated isocyanurates. In the other system, HOCl is in stoichiometric excess of HOBr. Although overall reaction rate is not affected by the halogen concentration, the product distribution is affected according to the relative amounts and rates for HOCl and HOBr. Therefore, in the bromide-spiked water, the addition of cyanuric acid would be expected to favor formation of more heavily brominated THM species to a greater extent than the non-cyanuric acid treated water and this was observed.

CONCLUSIONS

These studies show that cyanuric acid, when used in combination with 13 mg/L chlorine at an applied molar ratio greater than 1.1:1 or at pH less than 9, inhibited total trihalomethane formation by a mean 29% in filtered river water; at lower ratios cyanuric acid had little or no effect. In bromide-laden waters, cyanuric acid demonstrated only a 9% decrease in total trihalomethanes, but favored the formation of brominated over chlorinated

THM species. These data can be explained in part by the classical haloform reaction as a mechanism for THM formation.

It is not known whether a 9-29 percent reduction in total trihalomethane formation would occur at the concentrations at which chlorine is typically applied during water treatment, i.e., below 13 mg/L, or what the complicating effects of other treatment processes would be. Cyanuric acid probably holds little promise for trihalomethane control in drinking water treatment. Before cyanuric acid could be applied to potable water it would be necessary to undertake an extensive study of its potential health effects and to ensure that finished water microbial standards would be met.

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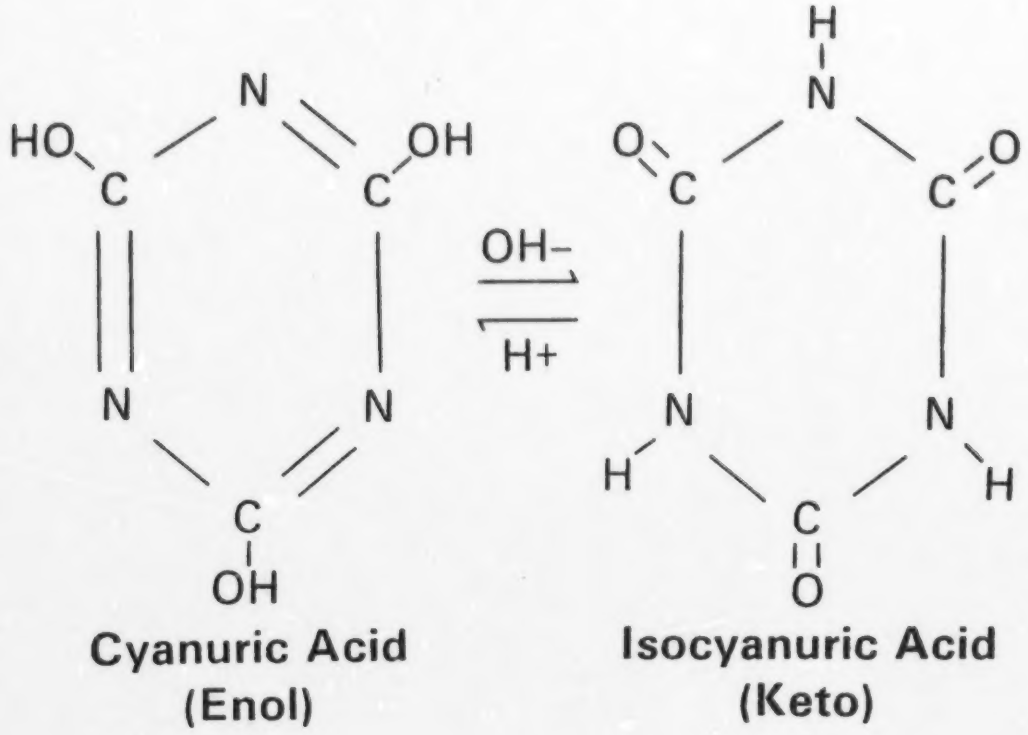

Figure 1. Tautomeric forms of cyanuric acid.

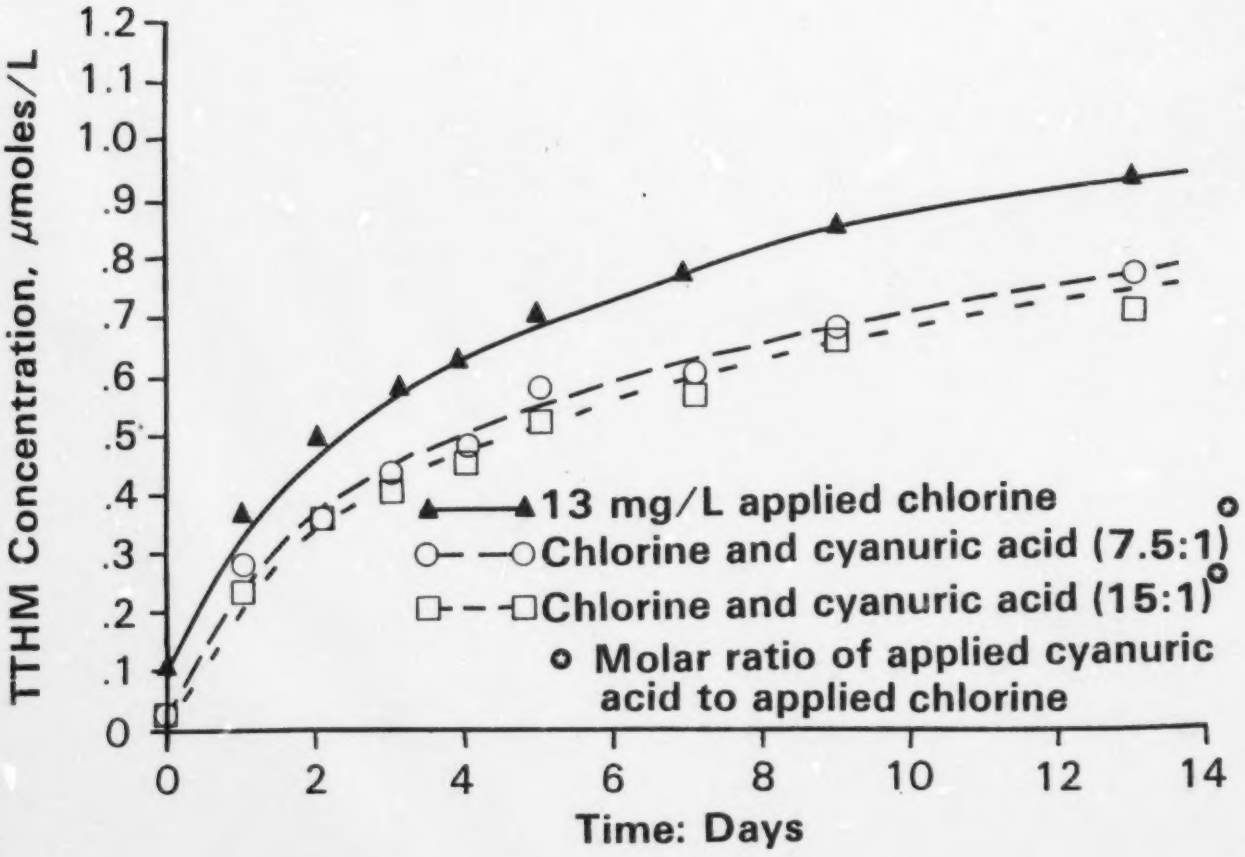

Figure 2. Effect of cyanuric acid on TTHM formation in river water.

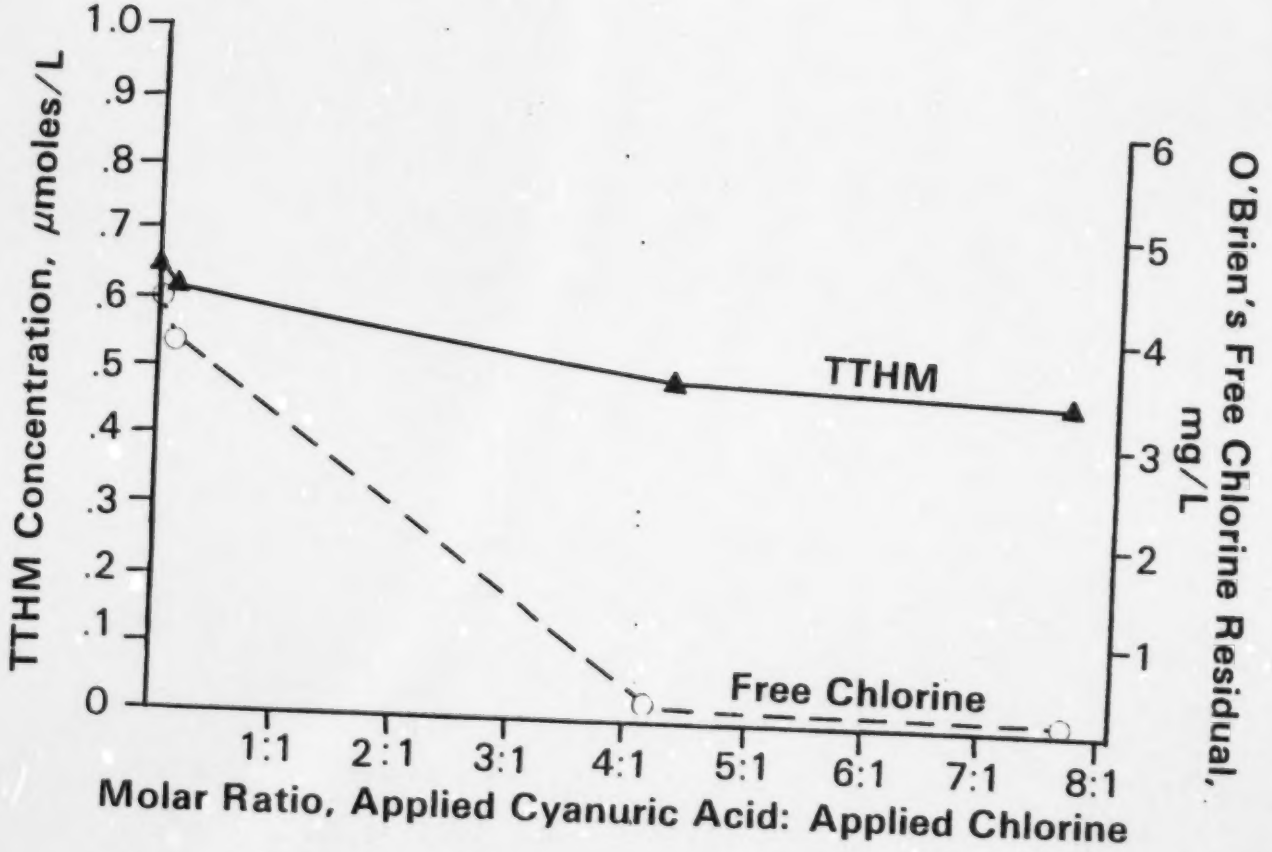

Figure 3. Effect of molar ratio on TTHM formation in river water after 7 days at pH 7.

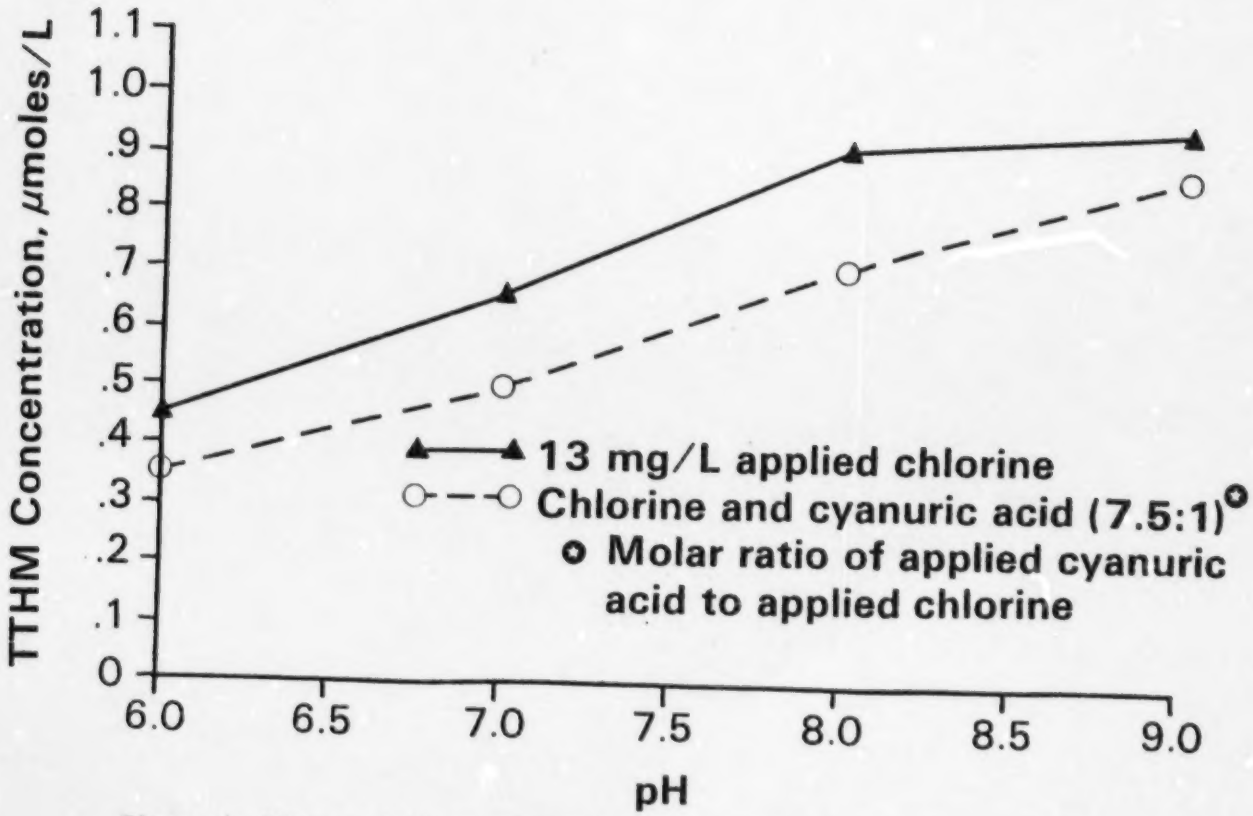

Figure 4. Effect of pH on TTHM formationin river water in the presence of cyanuric acid after 7 days.

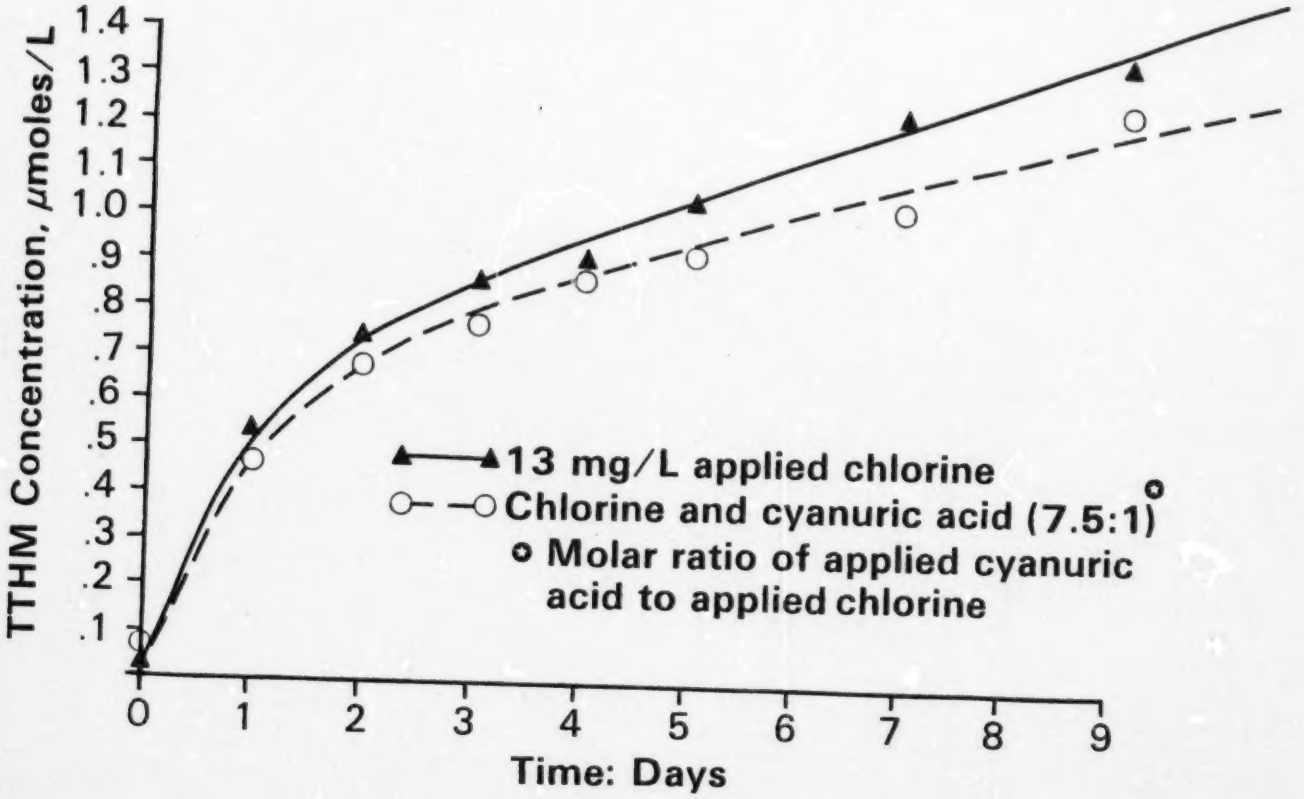

Figure 5. Effect of cyanuric acid on TTHM formation in bromide-spiked river water.

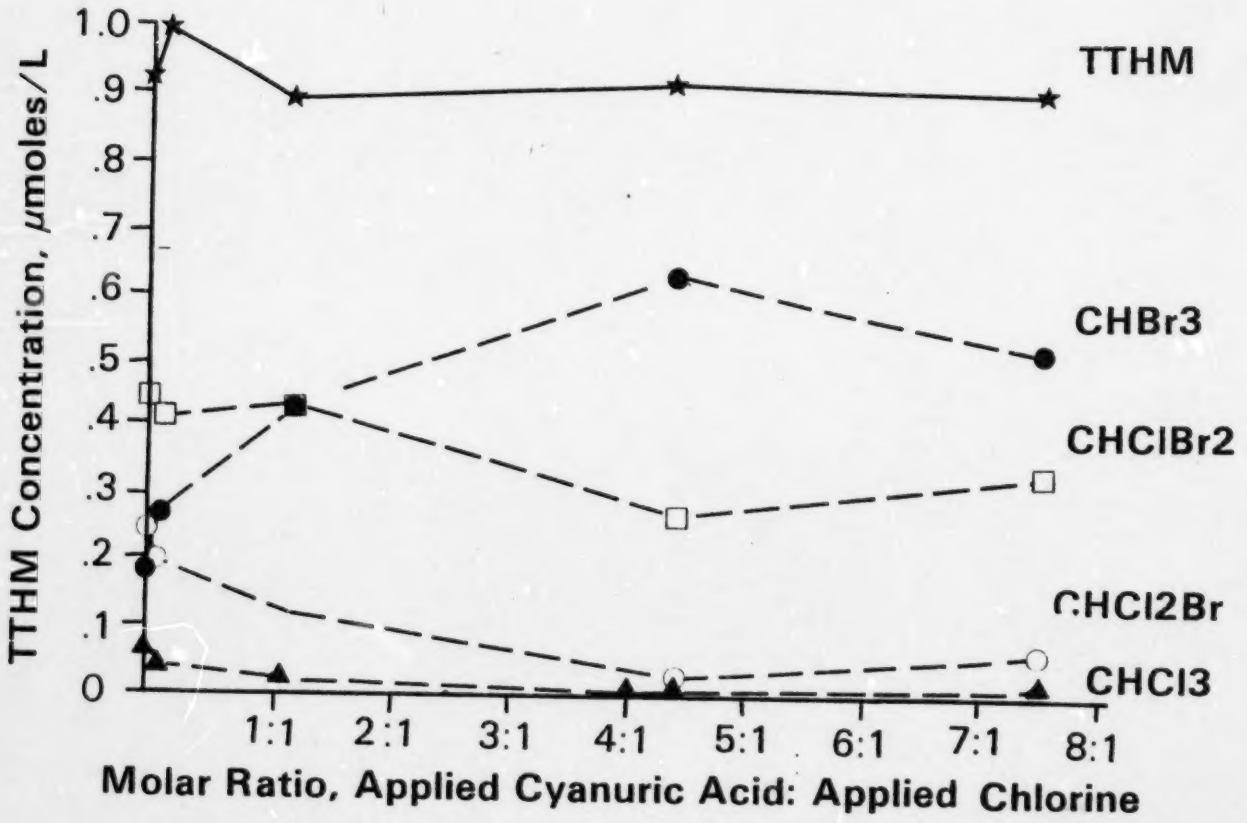

Figure 6. Effect of molar ratio on TTHM formation in bromide-spiked river water after 7 days at pH 7.

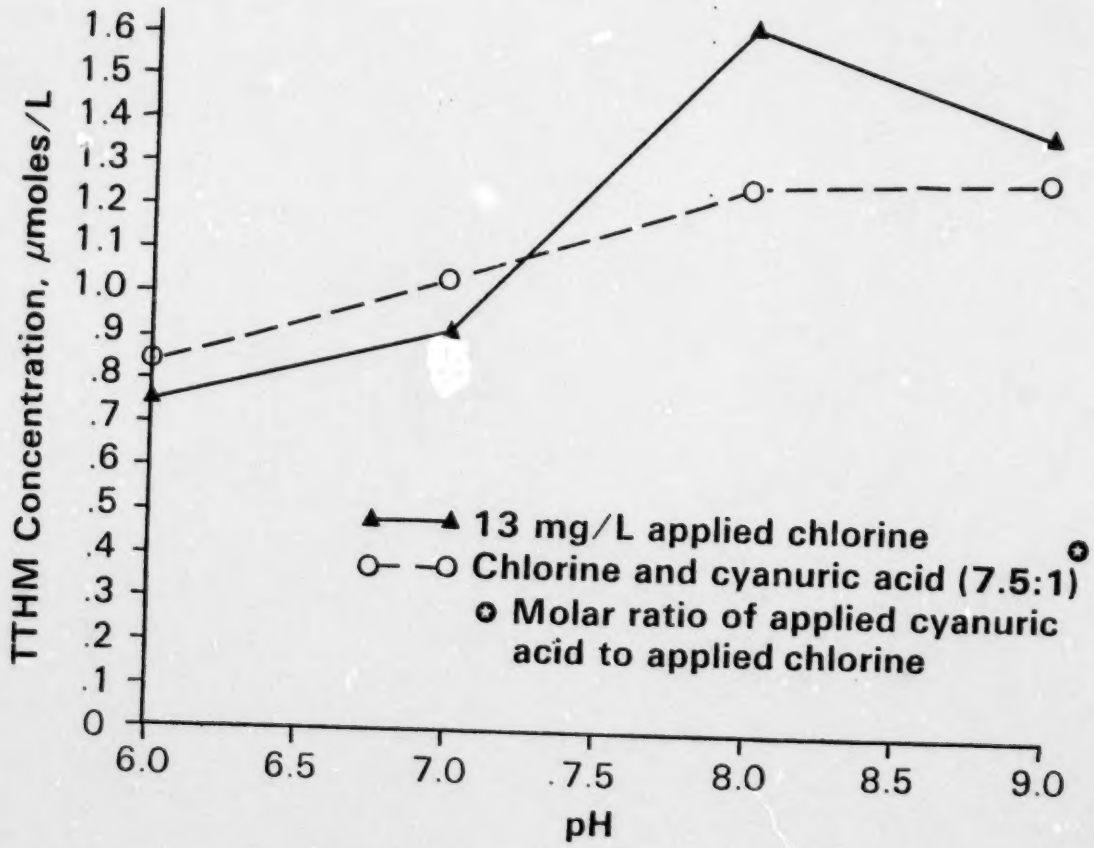

Figure 7. Effect of pH on TTHM formation in the presence of cyanuric acid in bromide-spiked river water after 7 days.